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Yaroslav B. Losovyj

*University of Nebraska-Lincoln*, [ylozovyy@indiana.edu](mailto:ylozovyy@indiana.edu)

Kevin Morris

*Louisiana State University, Baton Rouge, LA*

Luis G. Rosa

*University of Nebraska-Lincoln*, [luis.rosa13@upr.edu](mailto:luis.rosa13@upr.edu)

John D. Scott

*Louisiana State University, Baton Rouge*

Peter A. Dowben

*University of Nebraska-Lincoln*, [pdowben@unl.edu](mailto:pdowben@unl.edu)

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# High-resolution photoemission study of organic systems at the CAMD 3 m NIM beamline

Yaroslav Losovyj<sup>a, b, c</sup>, Kevin Morris<sup>a</sup>, Luis Rosa<sup>b</sup>, John D. Scott<sup>a</sup>, and Peter Dowben<sup>b</sup>

<sup>a</sup> Center for Advanced Microstructures and Devices, Louisiana State University,  
6980 Jefferson Highway, Baton Rouge, LA 70806, USA

<sup>b</sup> Department of Physics and Astronomy, Nebraska Center for Materials and Nanoscience,  
University of Nebraska–Lincoln, P.O. Box 880111, Lincoln, NE 68588-0111, USA

<sup>c</sup> Corresponding author: Center for Advanced Microstructures and Devices, Louisiana State University,  
6980 Jefferson Highway, Baton Rouge, LA 70806, USA. Tel. 225 578-9368; fax 225 578-6954; email: ylosovyj@lsu.edu

## Abstract

The 3 m normal incidence monochromator (NIM) VUV beamline at CAMD was designed for novel high-resolution photoemission experiments. Both solid-state samples and gas phase resolution tests demonstrate that high-resolution photoemission is possible below 10 meV, and vibronic fine structure in the photoemission final state from the crystalline copolymer poly-vinylidene fluoride with trifluoroethylene can be observed: the first direct experimental identification of symmetry dependence in electron–phonon coupling in photoemission from a solid-state system.

**Keywords:** High-resolution photoemission, Phonon–electron interactions, Franck–Condon scattering

## 1. Introduction

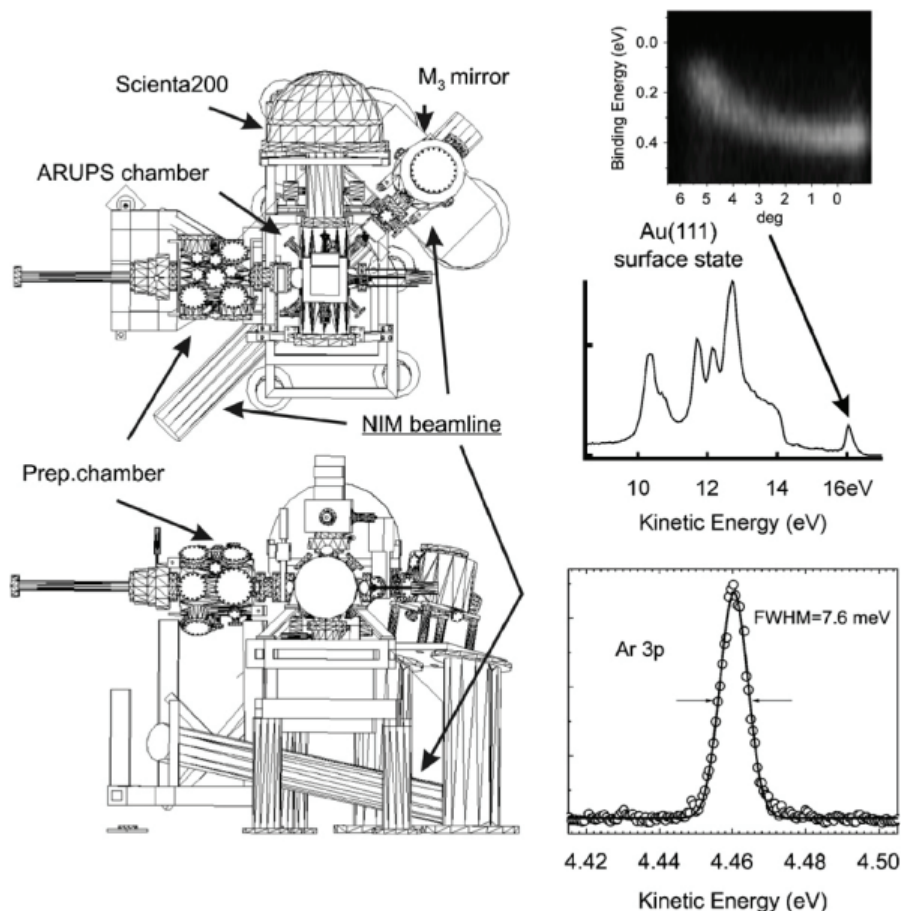
The 3m normal incidence monochromator (NIM) VUV beamline at CAMD was designed to deliver high resolution, high flux VUV synchrotron radiation for investigations in the basic and material surface science field. The beamline is equipped with an endstation consisting of two separate chambers consisting of a basic high resolution photoemission chamber connected through a sample transfer system with the sample preparation chamber.

We show here results, recently performed, of vibronic final states effects in photoemission of a solid-state organic system. These results provide evidence of a symmetry dependence in electron–phonon coupling in poly(vinylidene fluoride) (70%) and trifluoroethylene (30%).

## 2. Experimental details

The 3 m NIM beamline consists of a water-cooled ellipsoidal entrance mirror with a 70 mrad acceptance angle for horizontal radiation from a dipole magnet at CAMD. Two cylindrical mirrors produce a coma-free image on the entrance slit because of opposite sign comas for each mirror in the vertical direction. Two interchangeable gratings (Richardson Grating Laboratory, Rochester, NY) with different blaze angles and surface coatings are housed in a monochromator utilizing a McPherson mount [1], as described elsewhere [2].

This NIM is combined with an angle-resolved ultraviolet photoemission (ARUPS) endstation (as schematically indicated in Figure 1), which consists of a magnetic field shielded UHV chamber with an electron energy analyzer (Scienta SES200

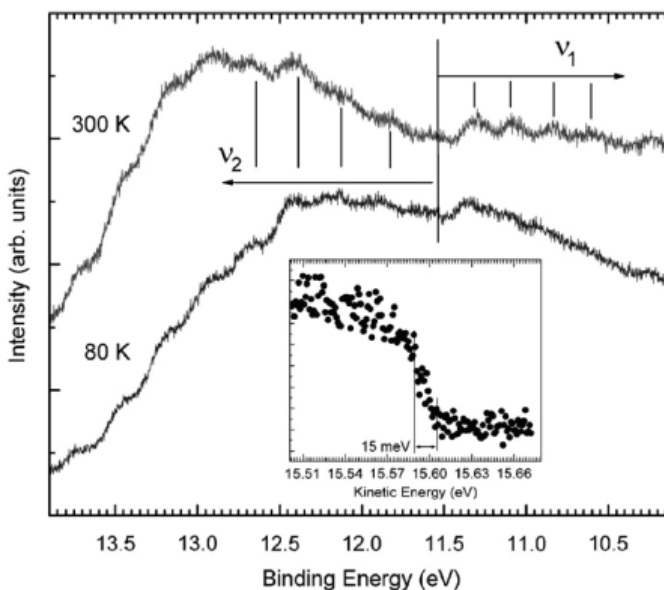


**Figure 1.** The layout of micro/nanofabrication and characterization system at 3 m NIM beamline at CAMD. Insets show angular mode test results for a Au(111) single crystal and the resolution tests for Ar gas phase target.

electron energy analyzer). The ARUPS chamber is connected to a preparation chamber equipped with capabilities for Low Energy Electron Diffraction/Auger Electron Spectroscopy/Scanning Tunneling Microscopy as well as sputtering/deposition/dosing facilities, by a 36 in. McAllister linear translator. Both chambers can be used independently and are equipped with sample holders providing heating/cooling capabilities. The polar rotation of the sample is accomplished by a differentially pumped rotary feed through with the liquid helium/liquid nitrogen cooled cryostat mounted on McAllister XYZ manipulator with a rotational accuracy is  $0.5^\circ$ . With the liquid He cooled cryostat, the sample temperature can be controlled from 30 to 450 K with approximately  $1^\circ$  accuracy.

### 3. Experimental results and discussion

Both gas phase resolution tests (see inset in Figure 1) and solid-state sample spectra (Figure 2) show that the demonstrated resolution is 9 meV or less for the combined beamline/electron analyzer (in transmission mode for the latter) for the Fermi edge of gold films on the silicon and better than 5 meV ultimate electron energy analyzer resolution for the Ar 3p level using



**Figure 2.** The first direct experimental identification of symmetry dependence in electron-phonon coupling in a solid-state system observed in the crystalline polymer P(VDF-TrFE) [4]. Inset shows the resolution tests using the Au Fermi edge, at 21 eV photon energy.

He I radiation. As it is seen from the inset in Figure 2, the measured Fermi edge broadening of gold films at  $\sim 30$  K at 12–88% of the step width is less than 15 meV. This corresponds to better than 9 meV combined analyzer/beamline resolution after deconvolution of the Fermi–Dirac distribution. Our gas phase results, with 500  $\mu\text{m}$  analyzer slits, show FWHM (7–8 meV) for the Ar gas 3p level. This comparable to reported previously for these Scienta SES200 electron energy analyzers at SSRL and ALS. The combination of the same 2 eV pass energy and the narrowest (200  $\mu\text{m}$ ) slit does not significantly improve the measured peak widths. Possible reasons of this limitation is much wider line width of our conventional He I radiation source compared to high-resolution microwave discharge VUV sources, or regular discharge sources employing space charge compensation electrodes. If one considers the Doppler broadening [3] of  $\sim 4.62$  meV for the Ar–He gas, this suggests a 6 meV combined analyzer/source resolution. Assuming a value of 4.3 meV broadening introduced by our conventional He I radiation source (the best sources have close to 1.2 meV line width), we estimate 4.2 meV for ultimate analyzer resolution. In the angular mode, the photoemission data both for a gold film on silicon and for a Au(1 1 1) single crystal show parabolic shaped dispersion of the well known gold surface state (see insets in Figure 1), which is consistent with expectations.

This relatively high combined resolution permits the identification of vibronic fine structure in the photoemission final state. We identified (see Figure 2) two different vibrational contributions to the photoemission fine structure of the ferroelectric copolymer poly(vinylidene fluoride) with trifluoroethylene, ( $\text{CH}_2\text{--CF}_2$ :  $\text{CHF--CF}_2$ , 70%: 30%) [3], as denoted in Figure 2. Surprisingly, the contribution of one

vibrational mode (denoted by  $\nu_1$  in Figure 2) to the photoemission fine structure decreases with decreasing temperature. We associate this temperature dependence to the importance of symmetry in vibronic coupling to the photoemission process and increased dipole ordering with decreasing temperature in this ferroelectric system, as noted elsewhere [4].

Studies like this one demonstrate that vibronic contributions to valence band photoemission of large *adsorbed* organic species are now possible using a synchrotron light sources [4], [5] and [6].

### Acknowledgements

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